

The Electronic Spectra of Thioamides and Thiohydrazides

Part I. LCAO-MO Treatment and Band Classification for Thiobenzamides

JAN SANDSTRÖM

Department of Organic Chemistry, University of Lund, Lund, Sweden

The ultraviolet spectra of thiobenzamide, N-methylthiobenzamide, and N,N-dimethylthiobenzamide have been recorded in different solvents. A long-wavelength, low-intensity maximum has been assigned to a $n \rightarrow \pi^*$ transition, and a maximum with higher intensity to a $\pi \rightarrow \pi^*$ transition. These assignments and the same ones for thioacetamide are supported by simple LCAO-MO calculations. For dimethylthiobenzamide a steric effect has been included in the calculations, and a prediction of the spectrum of thioacrylamide is given. S-protonation of thioamides in sulphuric acid is supported by NMR spectra.

The light absorption of organic thione compounds has been the subject of investigation for quite a long time due to the remarkable "chromophoric" properties of the thione group. As readily available thiones the thioamides have attracted a special interest. Hantzsch¹ showed by comparing the ultraviolet spectra of suitably substituted derivatives with those of the parent compounds that thioamides mainly occur as thiones and not as the tautomeric imidothiol forms. Burawoy^{2,3} made a systematic survey of the ultraviolet spectra of available thiones, and he found a characteristic long-wavelength, low-intensity band, which he called the R-band, and a more intense band, the K-band, at shorter wavelengths. The origin of the R-band has been a matter of dispute for some time³⁻⁵, but it is now fairly well established that the low-intensity band of the thiones is due to the excitation of a nonbonding electron from the sulphur atom to an antibonding π orbital, a $n \rightarrow \pi^*$ transition in the terminology proposed by Kasha⁵. The classification of $n \rightarrow \pi^*$ bands is mainly based on the effects of substituents and solvent polarity, and by such means it has recently been shown⁶⁻¹⁰ that the low-intensity bands in simple thioamides are also due to $n \rightarrow \pi^*$ transitions.

In his very thorough investigation of the ultraviolet spectra of organic thiones, Janssen⁶⁻⁸ has also included a number of thioamides. Regarding

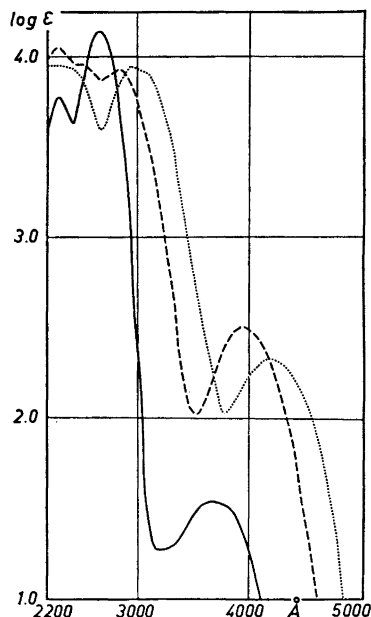


Fig. 1. Ultraviolet spectra of thioacetamide (—), thiobenzamide (.....), and N,N-dimethylthiobenzamide (-----) in heptane.

the classification of the strong band of thioacetamide at 2670 Å ($\log \epsilon$ 4.14, in heptane) he comes to two conflicting conclusions. His study of the solvent and substituent effects leads to the assignation of the band to a $n \rightarrow \sigma^*$ transition, whereas a LCAO—MO calculation gives better agreement if the band is assumed to be due to a $\pi \rightarrow \pi^*$ transition.

It was hoped that this uncertainty could be removed by an investigation of thioamides where the thioamide group was conjugated with an unsaturated system. A $\pi \rightarrow \pi^*$ transition should occur with lower energy due to the conjugation, whereas a $n \rightarrow \sigma^*$ transition should be less affected. Therefore, if the 2670 Å band is considerably shifted towards a longer wavelength by conjugation, it is probably a $\pi \rightarrow \pi^*$ band, but if it remains in the same region, it should be due to a $n \rightarrow \sigma^*$ transition. As a readily available conjugated thioamide thiobenzamide was chosen, and it was found that the 2670 Å band disappears when the thioamide group is conjugated with a phenyl ring. Instead, a new band appears at 2980 Å ($\log \epsilon$ 3.81, in heptane). However, it has been shown by Pullman¹¹ that enlargement of a conjugated system can sometimes lead to a hypsochromic shift instead of the expected bathochromic one. Therefore it was thought worthwhile to perform a LCAO—MO calculation on thiobenzamide in order to examine the effect of conjugation on the different energy levels. It is well known that the simple Hückel approximation often gives moderately reliable results only for the ground state properties, but the iterative procedure proposed by Wheland and Mann¹² has been of considerable value in the hands of Nagakura¹³ for the calculations involving excited levels, and the somewhat simplified procedure of Janssen⁸ gives

Table 1.

	Thioacetamide	Conjugate acid (I)	Thioacrylamide	Thiobenzamide	Dimethylthiobenzamide	
					(1)	(2)
Antibonding orbitals	$a - 1.209\beta$	$a - 0.972\beta$	$a - 2.092\beta$ $a - 0.782\beta$	$a - 2.781\beta$ $a - 1.797\beta$ $a - 1.333\beta$ $a - 0.795\beta$	$a - 2.783\beta$ $a - 1.810\beta$ $a - 1.333\beta$ $a - 0.819\beta$	$a - 2.688\beta$ $a - 1.539\beta$ $a - 1.333\beta$ $a - 1.059\beta$
Nonbonding orbital	$a + 0.029\beta$	—	$a + 0.055\beta$	$a + 0.051\beta$	$a + 0.027\beta$	$a + 0.009\beta$
Bonding orbitals	$a + 0.388\beta$ $a + 2.820\beta$	$a + 0.941\beta$ $a + 3.032\beta$	$a + 0.368\beta$ $a + 1.540\beta$ $a + 2.966\beta$	$a + 0.366\beta$ $a + 1.347\beta$ $a + 1.386\beta$ $a + 2.519\beta$ $a + 3.087\beta$	$a + 0.321\beta$ $a + 1.347\beta$ $a + 1.361\beta$ $a + 2.479\beta$ $a + 3.038\beta$	$a + 0.330\beta$ $a + 1.336\beta$ $a + 1.340\beta$ $a + 2.578\beta$ $a + 2.834\beta$
$\Delta E_{n \rightarrow \pi^*}$	-1.238 β	—	-0.837 β	-0.846 β	-0.846 β	-1.068 β
$\Delta E_{\pi \rightarrow \pi^*}$	-1.597 β	-1.913 β	-1.150 β	-1.161 β	-1.140 β	-1.389 β
Resonance energy *	-1.104 β	—	-2.436 β	-4.108 β	-4.176 β	-3.924 β

* -2β subtracted for the thiobenzamides. The value for the energy of the C=S bond, -2.312β , is taken from Ref.⁸

good agreement between calculated and found $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies for a number of different thiones. The method of Janssen can therefore be used with confidence at least to calculate the directions of the shifts imposed upon the energy levels of the thioamide group by conjugation. The calculations were carried out using an electronic digital computer, and the solutions of the secular equations and the calculations of new parameters were combined into one single program. The iterations were continued until $|p_m - p_{m-1}| < 4 \times 10^{-4}$ and $|q_m - q_{m-1}| < 2 \times 10^{-4}$ (p_m and q_m = bond order and charge in the m -th iteration). The Coulomb and resonance integrals are the same as those used by Janssen⁸.

The value of $\Delta E_{\pi-\pi^*}$ for thiobenzamide (Table 1) shows that the effect of conjugation actually is to shift the $\pi \rightarrow \pi^*$ band to a lower frequency. The numerical value of the shift is lower than expected from the calculated

Table 2.

$\nu_{\text{thioacetamide}}/\nu_{\text{thiobenzamide}}$		
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
Calc.	1.46	1.38
Found	1.14	1.12

Table 3.

Compound	Solvent	$n \rightarrow \pi^*$			$\pi \rightarrow \pi^*$			$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\Delta\nu^a \text{ cm}^{-1}$
		$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\Delta\nu^a \text{ cm}^{-1}$	$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\Delta\nu^a \text{ cm}^{-1}$			
CH_3CSNH_2	Heptane	3670 ^b	1.55 ^b	—	2670	4.14	—	2310	3.77	—
	Ethanol	3270	1.71	—	2660	4.10	—	2100	3.63	—
	Water	3090	1.88	—	2610	4.00	—	—	—	—
$\text{C}_6\text{H}_5\text{CSNH}_2$	Heptane	4180	2.33	3400	2980	3.81	3900	2390	3.94	1500
	CCl_4	4125	2.40	—	—	—	—	—	—	—
	Ethanol	3700 ^c	2.4	—	2960	3.85	—	2410	3.97	—
	Water ^d	3650 ^c	2.5	—	2870	3.93	—	2480	3.93	—
$\text{C}_6\text{H}_5\text{CSNHCH}_3$	Heptane	4020	2.48	2400	2880	3.81	2800	2370	4.04	1100
	CCl_4	3960	2.45	—	—	—	—	—	—	—
	Ethanol	3905	2.41	—	2865	3.86	—	2380	4.03	—
	Water ^d	3550 ^c	2.4	—	2750	3.92	—	2450	3.97	—
$\text{C}_6\text{H}_5\text{CSN}(\text{CH}_3)_2$	Heptane	3950	2.50	2000	2840	3.93	2600	2500	3.95	3300
	CCl_4	3890	2.56	—	—	—	—	—	—	—
	Ethanol	3660	2.47	—	2810	3.97	—	2390	3.99	—
	Water ^d	3520	2.47	—	2710	4.02	—	2300 ^c	4.0	—

^a $\nu_{\text{CH}_3\text{CSNH}_2} - \nu_{\text{PhCSNR}_1\text{R}_2}$, ^b Extrapolated value ^c Shoulder ^d With 5 % of ethanol.

transition energies of thioacetamide and thiobenzamide (Table 2), but the same applies to the $n \rightarrow \pi^*$ band and by no means invalidates the argument for the assignment of the 2670 Å band of thioacetamide to a $\pi \rightarrow \pi^*$ transition.

From Table 1 it is apparent that the energies of the highest bonding level and of the nonbonding level are only slightly raised, and therefore the bathochromic shifts of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands should mainly be due to the considerable decrease in energy of the lowest antibonding π level. If this is correct, the shift in frequency of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands when going from thioacetamide to thiobenzamide or its N-methyl derivatives ($\Delta\nu$ in Table 3) should be of the same magnitude. This is also the case. The $\Delta\nu$ values have been calculated for heptane solution only, because in ethanol and in water several of the $n \rightarrow \pi^*$ bands are so close to the $\pi \rightarrow \pi^*$ bands that the true positions of the maxima become uncertain, and furthermore the solvent-solute interaction should be as weak as possible, as is the case in heptane solutions.

The effect of methyl substitution on the nitrogen atom does not parallel the one found by Janssen for thioacetamide and several other simple thioamides. Instead, hypsochromic shifts are observed, when two methyl groups are successively introduced (Table 3). It is well known that methyl substitution increases the electron donating capacity of an amino group. This is borne out by the mesomeric dipole moments of the amino, methylamino, and dimethylamino groups, which are 1.67, 1.93, and 2.06 *D*, according to a recent determination by Smith¹⁴. In the calculations this effect can be accounted for in a simple

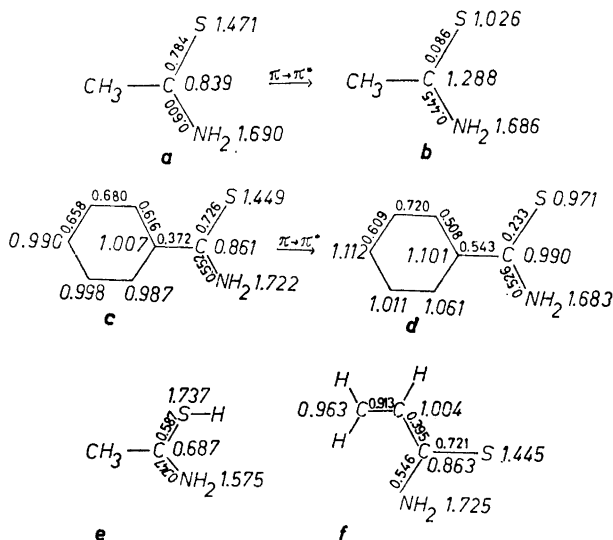


Fig. 2. π Electron distribution and π bond order of thioacetamide in ground state (a) and in excited state (b), thiobenzamide in ground state (c) and excited state (d), thioacetamidium ion in ground state (I, e), and thioacrylamide in ground state (f).

way by giving lower absolute values to the Coulomb integral for the nitrogen atom, when methyl groups are introduced. Janssen¹⁵ has shown that an increase in the electron-donating capacity of a hetero atom attached to a thione group will raise both the nonbonding level and the lowest antibonding π level. For thiobenzamide a calculation has now been performed with the Coulomb integral for nitrogen changed from $\alpha + 1.5\beta$ to $\alpha + 1.3\beta$. The results are found in Table 1, (1). It appears that the nonbonding and lowest antibonding levels are raised by the same amount of energy, but the highest bonding orbital is also raised, and the change in transition energy is negligible both for the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions. Thus the change in the Coulomb integral does not seem to account for the hypsochromic shifts on methyl substitution. An examination of the charge diagrams of the ground and excited states in a $\pi \rightarrow \pi^*$ transition (Fig. 2) shows that the inductive effect of the substituents on the nitrogen atom must have little effect on the energy of this transition both in thioacetamide and in thiobenzamide. This conclusion is based on the fact that the charge of the nitrogen atom is hardly affected by the transition. Therefore, as has been shown by Gerson and Heilbronner¹⁶, a change of the Coulomb integral is without effect on the energy of the transition. Instead, hyperconjugation and steric effects must be responsible for the shifts caused by alkyl substitution. An examination of molecular models reveals that the phenyl ring and the thioamide group in N,N-dimethylthiobenzamide cannot be coplanar (Fig. 3). If the steric repulsion is supposed to result in a rotation of the thioamide group out of the plane of

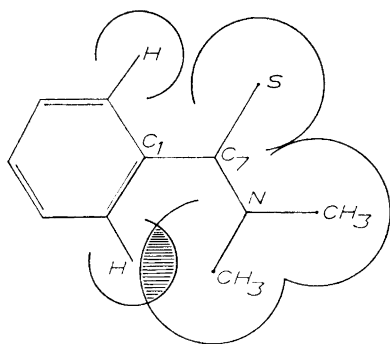


Fig. 3. Steric interference in *N,N*-dimethylthiobenzamide. As reasonable values for the radii of interaction 0.75 of the van der Waals radii have been chosen (for H 0.9 Å, for S 1.4 Å, and for CH₃ 1.5 Å). The C₇-N and C₇-S bond lengths have been taken from Ref.²⁰

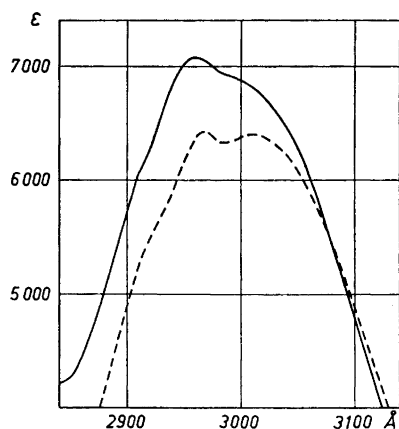


Fig. 4. Ultraviolet spectra of thiobenzamide in heptane (-----) and in ethanol (———).

the benzene ring, it can be taken into account in a calculation by lowering the absolute value of β for the corresponding bond in the secular equation, as has been shown by Heilbronner and Gerdil¹⁷ and by Coulson¹⁸. In order to find out the directions of the changes in the energy levels caused by a change in this integral, a calculation was performed on thiobenzamide with $\alpha_N = \alpha_C + 1.3\beta_{CC}$ and $\beta_{1,7} = 0.5\beta_{CC}$ (The C₁-C₇ bond connects the thioamide group with the benzene ring). The results of the calculation are found in Table 1 (2). The effect of the rotation is to increase the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies by about the same amounts (-0.22β and -0.25β). In harmony with this, the corresponding spectral shifts (from thiobenzamide to dimethylthiobenzamide) were found to be 1340 and 1650 cm⁻¹, in heptane. One of the common effects of steric inhibition of resonance is a lowering of the intensity of the affected absorption bands. This is found to be the case with the $\pi \rightarrow \pi^*$ band, for which the oscillator strength is lowered from 0.19 to 0.17 in heptane, whereas the oscillator strength for the $n \rightarrow \pi^*$ band increases from 0.0035 in thiobenzamide to 0.0046 in dimethylthiobenzamide. This increase is not surprising in view of the departure from coplanarity in the latter compound. It has been shown in several cases¹⁹⁻²¹ that the intensity of $n \rightarrow \pi^*$ transitions in ketones can be considerably increased if the lone pair orbital on the oxygen atom can overlap with a π orbital, which does not necessarily have to be in conjugation with the carbonyl group. However, the steric conditions must be such that the lone pair and π orbitals are not orthogonal, and the result is a partial mixing of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

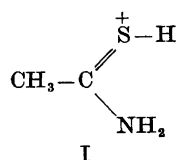
The oscillator strengths have been calculated with the aid of the simple formula $f = 4.31 \times 10^{-9} \times \epsilon_{\max} \times 2 (\nu_{\max} - \nu_{0.5})$, where $\nu_{0.5}$ is the wave number on the low frequency side of the band at which the extinction has gone down to half of the maximum value.

Thus it may well be that the increasing hypsochromic shifts caused by methyl substitution are due to increasing departure from coplanarity. Janssen⁶ has based a very reasonable explanation of the difference between the spectra of tetramethylthiourea and the other thioureas on a similar steric effect, but here the consequence of the departure from coplanarity is a bathochromic shift, since a heteroatom is turned out of conjugation.

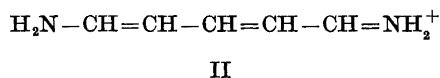
The energy levels, the π electron distribution and the bond orders of thioacrylamide have also been calculated in order to study the effect of a simpler kind of conjugation. As far as is known to the author, no simple α, β -unsaturated thioamide is described in literature. From the calculations (Table 1) it can be concluded that thioacrylamide should have its $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands very close to those of thiobenzamide.

The arguments which have been put forward by Janssen⁷ and by the present author⁹ in favour of a $n \rightarrow \sigma^*$ transition can be reinterpreted in the light of some new evidence to support a $\pi \rightarrow \pi^*$ transition. Like $n \rightarrow \pi^*$ transitions the $n \rightarrow \sigma^*$ transitions must undergo blue shifts when the solvent polarity is increased, since the excited state is less stabilized than the ground state with increasing solvation. This applies in particular to hydroxylic solvents, where hydrogen bonding to the nonbonding electrons is of overwhelming importance for the blue shift²². However, a $\pi \rightarrow \pi^*$ transition can also give rise to such a change in the distribution of the π electrons that a blue shift with increasing solvent polarity results. This must be the case when the polarity of a group, which is primarily responsible for the solvation, is considerably diminished or reversed during the transition. As has been pointed out by Janssen⁷ this occurs with the thione group in thioamides, and the same applies to thiobenzamide (Fig. 2). This effect must be smaller than the one caused by hydrogen bonding. Now the solvent shifts are of quite different magnitude for the low and high intensity bands in question. For thioacetamide the $n \rightarrow \pi^*$ band is shifted 3400 cm^{-1} and for thiobenzamide about 3100 cm^{-1} when going from heptane to ethanol. The corresponding shift for the high intensity band of thioacetamide is 140 cm^{-1} . For thiobenzamide the matter is somewhat complicated by a slight vibrational structure of the band in heptane (Fig. 4). As a rule the center of gravity of the band is used as the maximum value, but here it is evident that the solvent shift is best represented by the shift of the high frequency vibrational band, which amounts to 120 cm^{-1} . The solvent shifts of $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands should be of about equal magnitude, since the main effect of increasing the solvent polarity will be a lowering of the n level. This alone renders the assignment of the 2670 \AA band of thioacetamide to a $n \rightarrow \sigma^*$ transition somewhat doubtful. Furthermore, Janssen⁶ has shown that this band is shifted to 2340 \AA in concentrated sulphuric acid. As will be shown later, protonation in concentrated sulphuric acid occurs on the sulphur atom, and the nonbonding electrons in the free thioamide must be regarded essentially as σ electrons in the protonated species. They are therefore not available for transitions giving rise to absorption in

the near ultraviolet. A calculation has been performed to show the effect of S-protonation on the π levels of thioacetamide.



The calculations started with the form (I) and with the parameters $\alpha_{\text{C}} = \alpha$, $\alpha_{\text{S}^+} = \alpha + 1.5\beta$, $\alpha_{\text{N}} = \alpha + 1.5\beta$, $\beta_{\text{CS}} = 0.6\beta$, and $\beta_{\text{CN}} = 1.2\beta$. The final results are found in Table 1 and Fig. 2. Leroy²³ has shown that the iterative procedure gives a very reasonable result when starting with the form (II). In the final diagram both charge and bond order are symmetrically distributed, and there-



fore the method has also been applied with some confidence to the structure (I). It appears that the energy of the $\pi \rightarrow \pi^*$ transition is increased from -1.597β in thioacetamide to -1.913β in the protonated species, and therefore the band at 2340 Å may well be due to a $\pi \rightarrow \pi^*$ transition. From the excitation energies a $\pi \rightarrow \pi^*$ transition is calculated to appear at 2220 Å in the spectrum of the protonated species, so the agreement is reasonably satisfactory.

It is obvious that the results of the present investigation decidedly attribute the 2670 Å band of thioacetamide and the 2980 Å band of thiobenzamide to $\pi \rightarrow \pi^*$ transitions. This conclusion is further supported by a recent investigation by Hosoya *et al.*²⁴ As result of a semiempirical molecular orbital calculation with configuration interaction they assign the 2670 Å band to a $\pi \rightarrow \pi^*$ transition, and a second $\pi \rightarrow \pi^*$ transition is calculated to appear at 1670 Å. Despite the poor numerical agreement, this transition is assigned to a band at 2100 Å by means of measurements of the direction of the transition moment in the crystalline state.

Protonation of thioamides

The structure of the conjugate acids of the thioamides has been discussed by several authors with different results. Considerations of resonance stabilization would favour S-protonation, but arguments for N-protonation have also been put forward. Hosoya *et al.*²⁴ have concluded that N-protonation occurs, since S-protonation ought to raise the energy of the charge transfer state and thereby cause a bathochromic shift of the first $\pi \rightarrow \pi^*$ band. Instead, as mentioned above, a hypsochromic shift is found which is in harmony with the result of a simple calculation. However, Janssen²⁵ has criticized the theory of

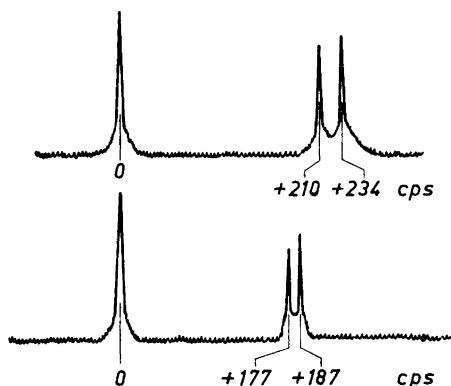


Fig. 5. NMR spectra of N,N-dimethylthiobenzamide in carbon tetrachloride (top) and sulphuric acid (bottom).

Hosoya *et al.* and presented convincing evidence from ultraviolet and infrared spectra of amides and thioamides and their conjugate acids, showing that O- and S-protonation occurs. During recent years a mass of evidence has been accumulated in support of O-protonation of amides, and in several cases (*e.g.* Refs.²⁶⁻²⁸) NMR spectra have been used to show that the rotation around the C—N bond is restricted, which would not have been the case, if N-protonation had occurred. The NMR spectrum has now been recorded for N,N-dimethylthiobenzamide in carbon tetrachloride and in concentrated sulphuric acid (Fig. 5). In both spectra two methyl signals are obtained, showing that the two methyl groups are differently disposed with respect to the thione group. Since N-protonation involves free rotation around the C—N bond, the spectra obtained are only compatible with S-protonation. The chemical shift between the methyl signals is changed from 24 cps in carbon tetrachloride to 10 cps in sulphuric acid. Cryoscopic determination of the van't Hoff *i*-factor in 100 % sulphuric acid shows that dimethylthiobenzamide is monoprotanated in this solvent (Table 4).

In hydroxylic solvents hydrogen bonding probably also occurs to the sulphur atom. Wheatley²⁹ and Penfold³⁰ have shown by X-ray crystallography and Hopkins and Hunter³¹ by association measurements that the sulphur atom is the basic center of intermolecular hydrogen bonds in thioamides. Flett³² has stressed the similarity in infrared spectra of associated thioamides and associated carboxylic acids, where the same type of bonding occurs.

Table 4. van't Hoff *i*-factors for N,N-dimethylthiobenzamide in 100 % sulphuric acid.

m	$\Delta t^{\circ}\text{C}$	<i>i</i>
0.02220	0.282	2.06
0.01298	0.160	2.00
0.02278	0.286	2.01
0.01618	0.208	2.09

EXPERIMENTAL

Thioamides. Thioacetamide was a commercial purissimum quality and was recrystallized twice from water without change in melting point (112–113°).

The thiobenzamides were obtained in good yields by reaction between carboxymethyl dithiobenzoate²³ and ammonia or the appropriate amines. Thiobenzamide was recrystallized from benzene and methyl- and N,N-dimethylthiobenzamide from benzene-heptane to constant melting point.

Solvents. Heptane was shaken first with concentrated sulphuric acid and then with water, dried with Drierite and distilled through a 60 cm Vigreux column.

Ethanol, 99.5 %, was refluxed with 1 % of sodium ethoxide for some hours and was then distilled through a 60 cm Vigreux column.

Spectra. The ultraviolet spectra were recorded with a Beckman DU spectrophotometer with photomultiplier attachment. In most cases the readings were followed down to 2150 Å and only in a few cases down to 2050 Å, since the increasing spurious light made the readings uncertain.

The 3670 Å band of thioacetamide in heptane could not be obtained in the pure solvent because of the poor solubility of the compound. Instead, the spectrum was recorded in 5 cm stoppered quartz cells with thioacetamide in pure carbon tetrachloride and in carbon tetrachloride-heptane mixtures (1:4, 2:3, 3:2, and 4:1 v/v). In all these solvents the maximum appeared at 3670 Å, which was therefore taken as the position of the maximum in pure heptane. The molar extinction coefficient at the maximum wavelength decreased gradually with increasing heptane concentration and a value of 35 for pure heptane was obtained by extrapolation.

The NMR spectra were recorded with a Varian Associates model V-4300-B high resolution NMR spectrometer operating at 40 Mc/s, and a flux stabilized 12" electromagnet from the same company. The magnetic sweep was calibrated with the modulated side band technique.

Cryoscopic measurements. Sulphuric acid containing a slight excess of anhydride was prepared by mixing the calculated amounts of 95–97 % sulphuric acid (Merck, pro analysis) and fuming sulphuric acid with 20 % of anhydride of the same quality. Water was then added in small portions until the horizontal part of the melting point curve was reached. The melting point depressions have been corrected for supercooling, and the calculations have been performed as described by Hammett and Deyrup²⁴. N,N-Dimethylthiobenzamide dissolves readily in this sulphuric acid even at a low temperature, and it is recovered unchanged when the solution is poured onto ice.

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